

Plasmonic atoms and plasmonic molecules

D.V. Guzatov and V.V. Klimov*

*P.N. Lebedev Physical Institute, Russian Academy of Sciences,
53 Leninsky Prospect, Moscow 119991, Russia*

(Dated: February 2, 2008)

Abstract

The proposed paradigm of plasmonic atoms and plasmonic molecules allows one to describe and predict the strongly localized plasmonic oscillations in the clusters of nanoparticles and some other nanostructures in uniform way. Strongly localized plasmonic molecules near the contacting surfaces might become the fundamental elements (by analogy with Lego bricks) for a construction of fully integrated opto-electronic nanodevices of any complexity and scale of integration.

PACS numbers: 78.67.-n 73.20.Mf 32.50.+d

*Electronic address: vklim@sci.lebedev.ru

I. INTRODUCTION

A technological break-through in the fabrication of nanodimensional clusters and other metallic nanoparticles gave rise to a development of such nano-technological and nano-optical branch as nanoplasmonics, which is of great interest to physicists, chemists, material engineers, IT specialists, and biologists. The nanoplasmonics deals with conduction electron liquid oscillations in metallic nanostructures and nanoparticles, and an interaction of those oscillations with light (plasmon-polariton) [1, 2]. Such studies are also aimed at the oscillations of a crystal lattice (SiC, for example) in the nanoparticles, whose interaction with light has much in common with the plasmon oscillations (phonon-polariton) [3].

The important feature of nanoplasmonic phenomena is the combination of a strong spatial localization and high-frequency (from ultraviolet to infrared) of electron oscillations. In its turn, strong localization leads to a giant enhancement of the local optical and electrical fields. These important features of plasmonic particles made it possible to discover quite a number of new effects. One of the most developed is the use of large local fields near plasmonic nanoparticles for enhancement of the Raman scattering cross-section. Recent experiments have shown that such an increase may achieve 10-14 orders of magnitude, which may help to resolve single molecules [4]-[7]. The local enhancement of the fields can also be used to increase the fluorescence intensity and to determine the structure of a single DNA strand without using the fluorescent labels [8]-[9]. By using the nanoparticles of more complex shape one can provide enhancement of both the absorption and the emission of light by natural and artificial fluorophores [10]. On the other hand, the plasmon nanoparticles are proposed to be used in nanolasers [11] and to stimulate plasmonic oscillations in nanoparticles by means of the optical emission (SPASER) [12]. Beside these new applications of the plasmonic nanoparticles, one can essentially increase the efficiency-cost ratio, for example, in solar batteries or light emitting diodes [13, 14] by using the achievements in nanoplasmonics. And finally, it is awaited that the nanoplasmonics will make it possible to create a new element base (Genuine Integrated Optics and Ultracompact Optical Components) for the computers and data processing equipment by taking an advantage of small dimensions of metallic nanoparticles and fast speed of optical processes [15].

An intricate spatial structure of the physical phenomena, which form the basis of nanoplasmonics, impedes a development of the latter. Very often, the numerical studies

do not allow one to explain the physics of the observed phenomena, while the analytical studies are mostly devoted to the case of spherical and spheroidal nanoparticles, which are very far from the synthesized nanostructures from the viewpoint of geometry and physics. Separate nanoparticles are often approximated by point dipoles. This permits one to explain several phenomena (for example, a propagation of plasmons in a chain of nanoparticles [16]). But as a whole, the physics of plasmonic oscillations in complex nanostructures and nanoparticles remains insufficiently studied, and to make progress in this field one needs new approaches and new ideas.

As one of such approaches we suggest that the plasmonic effects observed in clusters of nanoparticles should be described by the paradigm of plasmonic atoms and molecules, which has much in common with the paradigm of normal atoms and molecules. This would allow one to explain the complex phenomena of nanoplasmonics in terms of atomic and molecular physics, and to propose quite a number of new applications of the nanoplasmonics.

Within the framework of our approach we propose to treat the plasmonic oscillations of the connected nanoparticles as the plasmonic atoms. The plasmonic atoms are analogous, in a certain way, to the electron oscillations at the nanocrystal quantum dots, which are also often called the artificial atoms [17].

The bound states of plasmonic atoms in the clusters of nanoparticles are proposed to be called the plasmonic molecules, and finally, the plasmonic oscillations in the nanoparticle gratings are proposed to be called the plasmonic crystals. Such an approach seems to be efficient and useful as it follows from the strongly localized plasmonic oscillations recently discovered in the clusters of spherical nanoparticles [18, 19, 20]. These oscillations, being localized and of short-range, represent the plasmonic molecules, and on their basis it is possible to create different kinds of plasmonic nanostructures and to develop new nanodevices (optical nanosensors of single molecules, nanoelectromechanical systems (NEMS [21]), and even plasmonic computers).

II. PLASMONIC ATOMS

Let us consider in more detail the analogy between the plasmonic and ordinary atoms. In the simplest case of a hydrogen atom, the energy levels are defined by the Bohr equation

$$E_n = -\frac{E_1}{n^2}, \quad n = 1, 2, 3, \dots \quad (1)$$

where $E_1=13.55$ eV is the ionization energy of hydrogen atom. The wave function of an electron has the form, in this case:

$$\psi_{nlm}(r, \theta, \varphi) = Z_{nl}(r) Y_l^m(\theta, \varphi), \quad (2)$$

where Z_{nl} is the radial part of the wave function, and Y_l^m , the spherical harmonic. For example, in the case of the first excited (2P) atomic state, the expression for the radial function takes the form:

$$Z_{21}(r) = N_{21} \left(\frac{r}{r_B} \right) e^{-\frac{r}{2r_B}}, \quad (3)$$

where N_{21} is the normalized constant, and r_B , the radius of the first Bohr orbit. Function (3) is represented in Fig. 1.

In the case of a spherically symmetric plasmonic atom, i.e. the plasmonic oscillations in a metallic spherical nanoparticle of the radius R_0 , under the Drude dispersion law $\varepsilon(\omega) = 1 - (\omega_{pl}/\omega)^2$ (where ω_{pl} is bulk plasmon frequency), the spectrum of the plasmonic oscillations will take the form:

$$E_n = \hbar\omega_{pl} \sqrt{\frac{n}{2n+1}}, \quad n = 1, 2, 3, \dots \quad (4)$$

whereas the electric field potential, in respect to (4), will have the form corresponding to (2) with the radial wave function

$$Z_n = N_n \begin{cases} (r/R_0)^n, & r \leq R_0, \\ (R_0/r)^{n+1}, & r > R_0, \end{cases} \quad (5)$$

where $n = 1, 2, 3, \dots$ and N_n is some constant. Function (5) for the index $n = 1$ is illustrated in Fig. 1 by a dotted line. It is seen from this figure that wave functions of the ordinary and plasmonic atoms are similar. The spectra (1) and (4) also have much in common.

The plasmonic oscillations have similar properties in the other spherically symmetrical layered systems (nanomatreshka) [22] and spheroidal nanoparticles (nanorice) [23].

The resonant plasmonic frequencies and potentials of plasmonic atoms in more complex and less symmetrical nanoparticles have a more complex form. For example, in the case of a

metallic nanoparticle having a form of a three-axial ellipsoid with the semi-axes $a_1 > a_2 > a_3$, the plasmonic frequencies will be defined by the ratio [24]

$$\omega_{nm} = \frac{\omega_{pl}}{\sqrt{1 - \varepsilon_{nm}}}, \quad \varepsilon_{nm} = \frac{E_n^m(a_1) F_n'^m(a_1)}{E_n'^m(a_1) F_n^m(a_1)},$$

$$n = 1, 2, 3, \dots \quad m = 1, 2, \dots 2n + 1, \quad (6)$$

where E_n^m and F_n^m are the internal and external Lame functions [25], and a stroke denotes the derivative of function by its argument. The dependences of the resonant dielectric permeabilities for $n = 3$ are shown in Fig. 2 . The explicit expressions for eigen frequencies and eigen functions, e.g., for the case of $n = 3$ and $m = 7$, have the form (Guzatov, Klimov to be published)

$$\omega_{37} = \omega_{pl} \sqrt{\frac{(a_1 a_2 a_3)^3}{2} \left(\sum_{\alpha=1}^3 a_{\alpha}^{-2} \right) I_{123}},$$

$$\psi_{37} = C_{37}xyz, \quad (7)$$

where C_{37} is a constant ; and $I_{123} = \int_0^{\infty} \frac{du}{\{(u+a_1^2)(u+a_2^2)(u+a_3^2)\}^{3/2}}$.

The distribution of a surface charge for the plasmonic oscillations with $n = 3$ and $m = 7$ derived from Eq. (7) has the form depicted in Fig. 3 (Guzatov, Klimov to be published).

Even more complex properties characterize the cubic and polyhedral plasmonic atoms [26]-[31]. The spectrum of the cubic plasmonic atoms was studied in [26], and some of the first values take the form

$$\frac{E_n}{\hbar\omega_{pl}} = 0.46225, \quad 0.54473, \quad 0.58722, \quad 0.66372, \quad 0.74953, \quad 0.83918 \quad (8)$$

Figure 4 illustrates schematically the surface charge distribution for several states of a cubic plasmonic atom as found in [27]. The experiments studying the cubic plasmonic atoms in [31] proved to be in an agreement with the theoretical calculations.

It is very important that both the plasmonic atom wavefunction (electric potential) and the field intensity are changing within the whole volume of a nanoparticle and the adjacent space, despite the fact that the structure of plasmonic atoms may be rather complex. By analogy with that, the surface charge in any plasmonic atom changes noticeably over the whole nanoparticle surface. Such a smeared spatial structure of plasmonic atoms is their

characteristic feature, and can be used in quite a number of applications such as nanosensors of single molecules. However, as the distance between nanoparticles decreases they start to interact more intensively. And instead of the plasmonic atoms it is expedient to use the conception of plasmonic molecules to describe the plasmonic oscillations in the closely situated and strongly interacting nanoparticles. As in the case of ordinary atoms and molecules, the question about the existence of bound states of the plasmonic atoms emerges here first of all.

III. PLASMONIC MOLECULES IN A TWO-SPHERE CLUSTER

The evidence for the existence of bound states of the plasmonic atoms was first provided in [18, 19] by the example of a cluster of two closely situated spherical nanoparticles (Fig. 5).

Generally speaking, the plasmonic oscillations in the cluster of two nanoparticles were studied earlier too [32]-[37]. However, it was assumed, both explicitly and implicitly, that the bound states are not formed in such a cluster, and the interaction assumes a scattering of plasmonic atoms on each other with a respective splitting of energy levels, and hybridization of wave functions (potentials) of single plasmonic atoms [36, 37]. That was the reason why the plasmonic molecules had not been predicted earlier.

The discovered by us spectrum of the plasmonic oscillations in a cluster of two spherical nanoparticles is shown in Fig. 6 for the case of identical spheres ($R_1 = R_2 = R_0$). There are only symmetrical (T-modes) and antisymmetrical (L-modes) states of the scattering within the range of $\omega < \omega_{pl}/\sqrt{2}$ ($\varepsilon < -1$). They exist at any distance between the particles, and continuously transit into the respective states of the weakly interacting plasmonic atoms with the characteristics (4) and (5), within large distances between the nanospheres. Just those scattering states had become the subject of investigations in [32]-[37].

In the region of $\omega_{pl} \geq \omega > \omega_{pl}/\sqrt{2}$ ($0 > \varepsilon > -1$) the plasmonic oscillations may exist only at small distances between the nanoparticles, and correspond to the bound states of the plasmonic atoms and molecules (M-modes). Note that the existence of the plasmonic molecules is by no means connected with a quasistatic approximation, and the calculations made within the framework of the total system of Maxwell's equations, with account for retardation effects, provide evidence for the existence of plasmonic molecules in the case of a small gap as compared with the radii of spheres (Guzatov, Klimov unpublished).

The analogous spectra appear for higher azimuthal numbers m , although there are some peculiarities in the spectra of the unbound plasmonic atoms.

In the region of small distances between the nanospheres, the properties of the plasmonic molecules may be studied analytically within quasistatic approximation. For the Drude dispersion law, the spectrum of the plasmonic molecules takes the form:

$$\begin{aligned}\omega_m^M &= \frac{\omega_{pl}}{\sqrt{1 - \varepsilon_m^M}}, \\ \varepsilon_m^M &= -(M + m + \delta_m) \operatorname{acosh}(R_{12}/(2R_0)) + \dots \\ M &= 1, 2, 3, \dots \quad m = 0, 1, 2 \dots\end{aligned}\tag{9}$$

where R_{12} is the distance between the centers of spheres and

$$\begin{aligned}\delta_0 &= 1/2, \quad \delta_1 = -0.08578, \quad \delta_2 = -0.2639, \dots \quad \delta_\infty = -1/2, \\ \delta_m &= -\frac{1}{2} - \frac{1}{2m} + \frac{1}{8m^3} - \frac{1}{16m^5} + \frac{5}{128m^7} - \dots \quad (m > 0)\end{aligned}\tag{10}$$

The potential of the axis-symmetric ($m=0$) state of the plasmonic molecule in a space between the spheres ($-\eta_0 < \eta < \eta_0$) has the form:

$$\psi_{M,m=0} \approx \frac{\sqrt{\cosh \eta - \cos \xi}}{a} \left(\frac{1}{M} \sum_{n=0}^{M-1} \frac{\cosh((n+1/2)\eta)}{\cosh((n+1/2)\eta_0)} P_n(\cos \xi) - \frac{\cosh((M+1/2)\eta)}{\cosh((M+1/2)\eta_0)} P_M(\cos \xi) \right),\tag{11}$$

where P_n^m is the associated Legendre function and η, ξ , the bispherical coordinates

$$\begin{aligned}\coth \eta &= \frac{x^2 + y^2 + z^2 + a^2}{2az}, \quad \cot \xi = \frac{x^2 + y^2 + z^2 - a^2}{2a\sqrt{x^2 + y^2}}, \\ a &= \sqrt{R_{12}^2/4 - R_0^2},\end{aligned}\tag{12}$$

and where $\cosh \eta_0 = R_{12}/(2R_0)$.

For the antisymmetric unbound plasmonic atom we have respectively

$$\begin{aligned}
\omega_m^L &= \frac{\omega_{pl}}{\sqrt{1 - \varepsilon_m^L}}, \\
\varepsilon_m^L &= -(L + m - 1/2)^{-1} / \operatorname{acosh}(R_{12}/(2R_0)) + \dots \\
L &= 1, 2, 3, \dots \quad m = 0, 1, 2 \dots
\end{aligned} \tag{13}$$

and

$$\begin{aligned}
\psi_{Lm} &\approx \sqrt{\cosh \eta - \cos \xi} \\
&\times \frac{\sinh((L + m - 1/2)\eta)}{\sinh((L + m - 1/2)\eta_0)} P_{L+m-1}^m(\cos \xi) \cos(m\varphi).
\end{aligned} \tag{14}$$

In the case of large azimuthal numbers, $m \gg 1$, one can also find simple asymptotic equations for the spectra of plasmonic oscillations in a cluster of two spheres. This case is of importance for calculation of van der Waals forces between nanoparticles.

Consider in more detail a structure of the wave functions (electric potentials) of the plasmonic molecules. Figure 7 illustrates a wave function spatial distribution of a plasmonic molecule and unbound states of plasmonic atoms in the x - z plane.

Spatial structure of antisymmetrical (L-modes) and symmetrical (T-modes) wave functions of the unbound plasmonic atoms, in the axis-symmetrical case ($m = 0$) corresponds to the structure of wave functions of the isolated atoms. Namely, a positive charge lies in one part of a sphere, while a negative charge, which is equal to the positive one due to the electrical neutrality of spheres, lies in the opposite part of the latter. An interaction between the plasmonic atoms is reduced, in this case, to a charge re-distribution on opposite semi-spheres.

In the case of plasmonic molecules (symmetrical M-modes), the situation is the opposite, and both positive and negative charges are concentrated in a small region near a gap between the nanospheres. Far from the gap, the wave functions of plasmonic molecules practically vanish.

In the case of $m = 1$, where the wave functions have an angular dependence $\cos \varphi$ or $\sin \varphi$, the situation is analogous. The only difference is that the dipole moments of the unbound plasmonic atoms and molecules are directed along the x - or y -axis.

As a whole, the wave function of the plasmonic atoms remains more or less distributed over the volume of both nanospheres, whereas the plasmonic molecules are strongly localized

near the gap between the nanospheres in a region with a characteristic dimension of the order of the gap size with the maxima at spherical surfaces.

A strong localization of the plasmonic modes is also well seen in Fig. 8, which shows a distribution of the (surface) charge over a surface of spheres. To plot these distributions we have used a polar system of coordinates (ρ, θ) for each sphere in plane $y = 0$. The surface charge distribution was depicted with $\rho = R_0(1 + \tilde{\sigma}(\theta))$ polar curve where $\tilde{\sigma}(\theta)$ is the dimensionless surface charge density as a function of polar angle of corresponding sphere.

As the distance between the spheres increases, the localization of the plasmonic molecules decreases. At critical distance between the spheres the plasmonic molecules disappear, whereas the unbound atoms do not change.

The localization of plasmonic molecules and unbound plasmonic atoms is different, which defines their different dependence on the exciting radiation. The polarizability of the unbound plasmonic atoms is of the order of a nanosphere volume $\alpha \sim R_0^3$, and they effectively interact with the uniform external fields of the respective orientation and symmetry. And on the contrary, the plasmonic molecules have a comparatively small polarizability $\alpha \sim \Delta^3$, where Δ is the value of the gap between the spheres. As a result, the plasmonic molecules are weakly excited by the uniform optical fields (as compared to the unbound plasmonic states). On the other hand, the plasmonic molecules interact effectively with strongly inhomogeneous fields that are localized near the gap between the spheres. Such fields are produced by the atomic and molecular radiation near the gap. This makes the plasmonic molecules extremely perspective from the viewpoint of a development of nanosensors and elements of the nanodevices, which are sensitive to single molecules. Quite probably, that the SERS from single molecules [4]-[7] is due to their interaction with the plasmonic molecules. It seems that hot points in fractal structures (Shalaev's hot spots [38]) are also due to the plasmonic molecules.

IV. PLASMONIC MOLECULES IN MORE COMPLICATED SYSTEMS OF NANOPARTICLES

Above we considered the plasmonic molecules and unbound states of the plasmonic atoms formed in a cluster of two identical nanospheres. However, the plasmonic molecules may be formed within a much wider set of clusters of the nanoparticles. The only necessary

condition for the formation of plasmonic molecules is smallness of the gap between the nanoparticles of the finite volume as compared to their characteristic dimensions. The plasmonic molecules may also be formed in connected particles with two or more nanobubbles or dielectric nanospheres inside them (Fig. 9).

A. Cluster made from different nanospheres

First of all, the plasmonic molecules can exist in a cluster of two different nanospheres. Here the spectra and wave functions of unbound plasmonic atoms and plasmonic molecules are completely analogous to the case of identical nanospheres. If the distance between the spheres is small, then the plasmonic molecule spectrum may be written in the form:

$$\begin{aligned} & \left(\frac{\varepsilon_1(\omega) - \varepsilon_3}{\varepsilon_1(\omega) + \varepsilon_3} \right) \left(\frac{\varepsilon_2(\omega) - \varepsilon_3}{\varepsilon_2(\omega) + \varepsilon_3} \right) \\ & \approx \exp [(2N + 2m - 1)\Omega], \\ & N = 1, 2, 3, \dots \quad m \gg 1, \end{aligned} \quad (15)$$

where the parameter Ω can be found from the expression

$$\cosh \Omega = \frac{R_{12}^2 - R_1^2 - R_2^2}{2R_1R_2}, \quad (16)$$

and where ε_1 , ε_2 , ε_3 are the dielectric constants of the first and second spheres and the space between them, correspondingly.

For the dispersion law of Drude for both spheres it can be found from (15)

$$\begin{aligned} \omega_{Nm}^2 = & \frac{1}{4} (\omega_{pl,1}^2 + \omega_{pl,2}^2) \pm \frac{1}{4} \left\{ (\omega_{pl,1}^2 - \omega_{pl,2}^2)^2 \right. \\ & \left. + 4\omega_{pl,1}^2\omega_{pl,2}^2 \exp [-(2N + 2m - 1)\Omega] \right\}^{1/2}, \end{aligned} \quad (17)$$

where $\omega_{pl,1}$ and $\omega_{pl,2}$ are the bulk plasmon frequencies of spheres.

B. Cluster made of two nonspherical particles

Strong localization of plasmonic molecules allows one to suggest that their characteristics depend mainly on the radius of curvature of almost contacting surfaces and the distance

between the centers of the inscribed (or circumscribed) spheres. So, for any smooth non-spherical particle the properties of plasmonic molecules formed in the gap may be estimated by considering the plasmonic molecules in two spheres, which approximate the nonspherical particles in the contact point (see Fig. 10).

For the closely set semi-infinite bodies the situation turns to be more intricate, since in this case part of the charges may go arbitrary far from the contact area. Nevertheless, here exist a localized plasmonic oscillations, which are analogous to the antisymmetric unbound plasmonic atoms (L-modes) and plasmonic molecules (M-modes).

In case of closely set semi-infinite hyperboloids (Fig. 11a) the variables in Laplace equation can be separated within prolate spheroid coordinates [39], and the localized plasmonic oscillation spectra have the form

$$\begin{aligned}\omega_m^L &= \omega_{pl} \left\{ P'_{-1/2+iL}{}^m(\mu_0) (P_{-1/2+iL}^m(-\mu_0) - P_{-1/2+iL}^m(\mu_0)) \right. \\ &\quad \times (P'_{-1/2+iL}{}^m(\mu_0) P_{-1/2+iL}^m(-\mu_0) \\ &\quad \left. + P'_{-1/2+iL}{}^m(-\mu_0) P_{-1/2+iL}^m(\mu_0))^{-1} \right\}^{1/2}, \\ \omega_m^M &= \omega_{pl} \left\{ P'_{-1/2+iM}{}^m(\mu_0) (P_{-1/2+iM}^m(-\mu_0) + P_{-1/2+iM}^m(\mu_0)) \right. \\ &\quad \times (P'_{-1/2+iM}{}^m(\mu_0) P_{-1/2+iM}^m(-\mu_0) \\ &\quad \left. + P'_{-1/2+iM}{}^m(-\mu_0) P_{-1/2+iM}^m(\mu_0))^{-1} \right\}^{1/2},\end{aligned}\quad (18)$$

where $m = 0, 1, 2, \dots$ and the indices L, M , which characterize the modes, continuously vary from 0 to the infinity; $\mu_0 = d/f$ (d is half of the smallest distance between the hyperboloids and f is half of the distance between the hyperboloids' focuses). The corresponding wave functions (electric potentials) in the gap ($-\mu_0 < \mu < \mu_0$) are

$$\begin{aligned}\psi_m^{(L)} &= P_{-1/2+iL}^m(\eta) (P_{-1/2+iL}^m(\mu) - P_{-1/2+iL}^m(-\mu)), \\ \psi_m^{(M)} &= P_{-1/2+iM}^m(\eta) (P_{-1/2+iM}^m(\mu) + P_{-1/2+iM}^m(-\mu)),\end{aligned}\quad (19)$$

where the prolate spheroid coordinates η, μ are related with the Cartesian coordinates by the equations

$$\begin{aligned}
(\eta - \mu) f &= \sqrt{R^2 + f^2 - 2fz}, \\
(\eta + \mu) f &= \sqrt{R^2 + f^2 + 2fz}, \\
R^2 &= x^2 + y^2 + z^2.
\end{aligned} \tag{20}$$

Inside the hyperboloids the expressions for wave function of plasmonic atoms and plasmonic molecules are analogous to (19).

The axis-symmetrical ($m = 0$) spectra for several values of L , $M = 1, 3, 5, 10$ are shown in Fig. 11b as functions of distance between hyperbolic tips. The spatial distribution of corresponding wavefunctions (electric potentials) for $L, M = 1$ are given in Fig. 12.

As seen from the figures, for both the symmetrical and antisymmetrical plasmonic oscillations there is observed a strong localization of the modes, and this ensures an effective interaction with the ordinary atoms, molecules or quantum dots with plasmonic atoms and molecules near the gap between tips. One more interesting fact is that the spectra of these oscillations are quite close to the oscillations in a two-sphere cluster. This allows one to consider the localized plasmonic oscillations in the gap between semi-infinite bodies as the virtual plasmonic atoms and molecules.

V. POSSIBLE APPLICATIONS OF PLASMONIC MOLECULES

Obviously, strong localization of plasmonic molecules may be suitable for a number of applications. This is particularly important when one needs to ensure effective interaction between the nanolocalized light sources (molecules and nanocrystal quantum dots) and the nanoparticles and nanostructures, as well as the nano-electromechanical devices [21], in which the van der Waals forces play an important role [40, 41].

A. The effect of the plasmonic molecules on the van der Waals forces (V.V. Klimov, A. Lambrecht to be published)

As is well known, the van der Waals forces are associated with spatial dependence of the vacuum fluctuation energy density. If the distance between the plasmonic nanoparticles is

small, then the main contribution to the van der Waals energy comes from zero (vacuum) oscillations of the plasmonic modes, i.e. the plasmonic atoms and molecules [42].

In case of two identical plasmonic nanospheres the contribution to the van der Waals energy comes from zero oscillations of the antisymmetric and symmetric unbound plasmonic atoms (L- and T-modes) and plasmonic molecules (M-modes)

$$\begin{aligned} U_{vdW} &= U_{vdW}^M + U_{vdW}^L + U_{vdW}^T \\ &= \frac{\hbar}{2} \left\{ \sum_{M=1}^{\infty} \omega_0^M + \sum_{L=1}^{\infty} \omega_0^L + \sum_{T=1}^{\infty} \omega_0^T \right\} \\ &\quad + \hbar \left\{ \sum_{M,m=1}^{\infty} \omega_m^M + \sum_{L,m=1}^{\infty} \omega_m^L + \sum_{T,m=1}^{\infty} \omega_m^T \right\}. \end{aligned} \quad (21)$$

In spite of the fact that the expressions for the van der Waals energy of different modes are formally similar, the noted contributions result in totally different physical consequences. Figure 6 shows that the energy of antisymmetric unbound states of the plasmonic atoms grows with distance, and this results in the particle attraction. In a similar manner, the energy of the plasmonic molecules diminishes with distance, and thus results in the repulsion of the nanospheres. Symmetric states of unbound plasmonic atoms also lead to a very weak repulsion.

The attraction or repulsion conditioned by different plasmonic oscillations is of a simple physical nature. First consider the axis-symmetrical oscillations ($m = 0$). Here the longitudinal antisymmetric modes are conditioned by the oscillations of the parallel dipoles which are attracting in accordance with the law of electrostatics (see Fig. 13 and Fig. 7). In case of symmetrical oscillations the dipoles have opposite directions, and this results in the dipole repulsion (see Fig. 13 and Fig. 7).

For $m = 1$, i.e. when the wave functions are described by the law of $\cos \varphi$ or $\sin \varphi$ (φ is the angle describing the rotation around symmetry axis), the directions of the dipoles corresponding to different plasmonic states are changed. For antisymmetric modes the dipole moments in different spheres should be crosswise to the symmetry axis and should have opposite orientations (Fig. 13 and Fig. 7). It is easily seen that this results again in the effect of attraction of the unbound plasmonic atoms. For the plasmonic molecules the dipole momenta should also be crosswise to the symmetry axis, but, due to the symmetry

with respect to z coordinate, should have the same direction (see Fig. 13). This again leads to the repulsion of nanospheres with plasmonic molecules.

Fig. 14 illustrates the dependence of the contributions from different plasmonic states into the van der Waals energy on the distance between the spheres. This was obtained by direct summation of all the plasmonic modes in (21). As it was clear beforehand, the symmetric modes lead to the repulsion, while the longitudinal antisymmetric modes lead to the attraction of the nanoparticles. Unexpectedly, the repulsion contribution from plasmonic molecules is almost equal to the attraction contribution of the unbound plasmonic atoms. As a result, the total van der Waals energy grows with distance, i.e. it is the attraction energy, but the amount of this energy is by an order smaller than the energy to be obtained without taking into account the contribution from the plasmonic molecules.

Direct measurement of the van der Waals force between the plasmonic nanoparticles may form the basis of the experimental proof of the plasmonic molecule existence.

B. The effect of plasmonic molecules on the emission of ordinary molecules and quantum dots

Since the plasmonic molecules particularly effectively interact with highly inhomogeneous electric fields, then one can develop different detectors of the ordinary single molecules or quantum dots. Fig. 15 illustrates the dependence of the radiation decay rate of spontaneous emission of different molecules, which fall within the gap between the two spheres, on the radiation wavelength. It is assumed that the nanospheres are made of Na with the plasmonic resonances in the visible range (Fig. 15a) or SiC with the phonon-polariton resonances in the IR range (Fig. 15b). The peaks in the right-hand part of the figures correspond to the interaction of an ordinary molecule and the unbound plasmonic atoms, while the peaks in the left-hand part correspond to the interaction with the plasmonic molecules.

The analysis of the figures shows that, similar to the case of the van der Waals energy, the interaction with plasmonic molecules is of greater importance than that with the symmetric unbound plasmonic atoms. Of fundamental importance is the fact that in a homogeneous external field the plasmonic molecules are not effectively excited. This results in the following: the clusters of two and more nanoparticles (where the geometry allows one to excite the plasmonic molecules of a certain frequency), can be used in the development of effective

nanodetectors of single molecules of high signal/noise ratio, since the external fields at the plasmonic molecule frequency fail to excite the plasmonic molecule effectively.

On the other hand, the effective interaction between the plasmonic and ordinary atoms and molecules can be applied both to the development of SPASER and single atom nanolaser, and the sets of such devices.

C. Large cluster or infinite array of nanoparticles

Probably, the most interesting consequence of the plasmonic molecule strong localization near the gap between the nanoparticles of arbitrary shapes lies in possible existence of plasmonic molecules in the clusters with more than two particles. Figure 16 illustrates a cluster of nine metallic nanoparticles, in which different configurations of plasmonic molecules may exist. In each of the twelve gaps a plasmonic molecule having the properties defined by the curvature radii of the closest surfaces and given by expressions (9)-(11) may be excited. In this system one can also excite the pairs, triples, quadruples, etc., of plasmonic molecules. Under simultaneous excitation of several plasmonic molecules a weak interaction between the molecules may be easily taken into account using the perturbation theory. The account for such an interaction results in the hybridization of the wave functions of single plasmonic molecules and a corresponding splitting of the spectrum. Similar reasoning is also fully applicable to the large-size arrays of nanoparticles, and this allows one to speak about plasmonic molecular crystals. In other words, a strong spatial localization of plasmonic molecules and their weak interaction with each other allows an almost linear scaling of any simpler structure of plasmonic molecules. To put it in simpler words, the plasmonic molecules allow one, similar to the Lego bricks, to produce the optoelectronic nanodevices of any complexity.

In principle, the excitation of plasmonic molecules in the clusters and arrays may be performed with the help of homogeneous optical fields of a corresponding resonant frequency. However, such a method of excitation is not highly effective due to weak polarizability of plasmonic molecules. A positive feature of such inefficiency is a weak sensitivity of plasmonic molecules to the external noise fields. A more effective method to excite the plasmonic molecules lies in the excitation by means of spontaneous or stimulated radiation (SPASER [12]) of usual molecules at a frequency of plasmonic molecule oscillation . In this case, depending on the orientation and location of the ordinary molecules (or nanocrystal quantum

dots) with respect to the exciting field, the plasmonic molecules may be produced in the given part of a cluster or array, and, thus, to produce different initial conditions for the data processing and transfer.

VI. CONCLUSION

In this work the analysis has been made of the plasmonic oscillations in single nanoparticles and the clusters of nanoparticles. It has been shown that all the plasmonic oscillations may be classed by the degree of their localization. Such oscillations where the localization is mostly defined by the size of single nanoparticles we propose to name "the plasmonic atoms", and those strongly localized in the nanoparticle contact zones (without electrical contact) we propose to name "the plasmonic molecules", since they are the bound states of plasmonic atoms. It has been demonstrated that the plasmonic molecules almost do not interact between each other, and, so, can form the structures of arbitrary spatial complexity. The methods of plasmonic molecule excitation and its applications in the description of NEMS and the nanodetectors of single molecules are briefly discussed as well.

Acknowledgments

The authors are grateful to the Russian Foundation for Basic Research (grants 05-02-19647 and 07-02-01328) and the Russian Academy of Sciences and Centre de Recherche Scientifique (France) for financial support of this work.

One of the authors (D.V.G.) is thankful to the Young scientists support Program of the Educational-Scientific Center of P.N. Lebedev Physical Institute and the RAS Presidium Program "Support of young scientists" for a partial financial support of the work.

- [1] H. Raether: *Surface Plasmons* (Springer-Verlag Berlin 1998)
- [2] U. Kreibig, M. Vollmer: *Optical Properties of Metal Clusters* (Springer-Verlag Berlin 1995)
- [3] R. Hillenbrand, T. Taubner, F. Keilmann: *Nature* 418, 159 (2002)
- [4] M. Moskovits, L.-L. Tay, , J. Yang, T. Haslett: *Top. Appl. Phys.* 82, 215 (2002)

[5] Z. Wang, S. Pan, T.D. Krauss, H. Du, L.J. Rothberg: Proc. Natl. Acad. Sci. USA 100, 8638 (2003)

[6] S. Nie, S.R. Emory: Science 275, 1102 (1997)

[7] A.M. Michaels, M. Nirmal, L.E. Brus: J. Am. Chem. Soc. 121, 9932 (1999)

[8] J.R. Lakowicz, J. Malicka, I. Gryczynski, Z. Gryczynski, C.D. Geddes: Phys. D: Appl. Phys. 36, R240 (2003)

[9] J.R. Lakowicz, B. Shen, Z. Gryczynski, S. D'Auria, I. Gryczynski: Biochem. Biophys. Res. Commun. 286, 875 (2001)

[10] D.V. Guzatov, V.V. Klimov: Chem. Phys. Lett. 412, 341 (2005)

[11] I.E. Protsenko, A.V. Uskov, O.A. Zaimidoroga, V.N. Samoilov, E.P. O'Reilly: Phys. Rev. A 71, 063812 (2005)

[12] D.J. Bergman, M.I. Stockman: Phys. Rev. Lett. 90, 027402 (2003)

[13] H. Benisty, H. de Neve, C. Weisbuch: IEEE Quantum Electron. 34, 1632 (1998)

[14] S. Curtis: Energy start-ups bank on nanotechnology <http://nanotechweb.org> (2005)

[15] S.I. Bozhevolnyi, A. Boltasseva, T. Nikolajsen, K. Leosson, K. Kjaer, M.S. Larsen: Lightwave Technology 23, 413 (2005)

[16] S.A. Maier, M.L. Brongersma, P.G. Kik, S. Meltzer, A.A.G. Requicha, H.A. Atwater: Adv. Mater. 13, 1501 (2001)

[17] A.P. Alivisatos: Science 271, 933 (1996)

[18] V.V. Klimov, D.V. Guzatov: Phys. Rev. B 75, 024303 (2007)

[19] V.V. Klimov, D.V. Guzatov: Kvantovaya elektronika [in Russian] 37, 209 (2007)

[20] V.V. Klimov, D.V. Guzatov: Nature (submitted)

[21] K.L. Ekinci, M.L. Roukes: Rev. Sci. Instrum. 76, 061101 (2005)

[22] C. Radloff, N.J. Halas: Nano Lett. 4, 1323 (2004)

[23] H. Wang, D.W. Brandl, F. Le, P. Nordlander, N.J. Halas: Nano Lett. 6, 827 (2006)

[24] O. Reese, L.C. Lew Yan Voon, M. Willatzen: Phys. Rev. B 70, 075401 (2004)

[25] E.W. Hobson: The Theory of Spherical and Ellipsoidal Harmonics (Cambridge University Press Cambridge 1931)

[26] R. Fuchs: Phys. Rev. B 11, 1732 (1975)

[27] U. Hohenester, J. Krenn: Phys. Rev. B 72, 195429 (2005)

[28] I.O. Sosa, C. Noguez, R.G. Barrera: Phys. Chem. B 107, 6269 (2003)

- [29] C. Noguez: Opt. Mat. 27, 1204 (2005)
- [30] C. Noguez: Phys. Chem. C, DOI: 10.1021/jp066539m (2007)
- [31] L.J. Sherry, S.-H. Chang, G.C. Schatz, R.P. Van Duyne, B.J. Wiley, Y. Xia: Nano Lett. 5, 2034 (2005)
- [32] F. Claro: Phys. Rev. B 25, 7875 (1982)
- [33] R. Ruppin: Phys. Rev. B 26, 3440 (1982)
- [34] I. Olivares, R. Rojas, F. Claro: Phys. Rev. B 35, 2453 (1987)
- [35] R. Ruppin: J. Phys. Soc. Japan 58, 1446 (1989)
- [36] P. Nordlander, C. Oubre, E. Prodan, K. Li, M.I. Stockman: Nano Lett. 4, 899 (2004)
- [37] H. Wang, D.W. Brandl, P. Nordlander, N.J. Halas: Acc. Chem. Res., DOI: 10.1021/ar0401045 (2006)
- [38] K. Seal, M.A. Nelson, Z.C. Ying, D.A. Genov, A.K. Sarychev, V.M. Shalaev: Phys. Rev. B 67, 035318 (2003)
- [39] W.R. Smythe: Static and dynamic electricity (McGraw-Hill London 1950)
- [40] I.E. Dzyaloshinskii, E.M. Lifshitz, L.P. Pitaevskii: Uspheki Fiz. Nauk [in Russian] 73, 381 (1961)
- [41] E.M. Lifshitz: Zh. Eksp. Teor. Phys. [in Russian] 2, 73 (1956)
- [42] F. Intravaia, A. Lambrecht: Phys. Rev. Lett. 94, 110404 (2005)
- [43] E.D. Palik (ed): Handbook of Optical Constants of Solids (Academic Press New York 1985)
- [44] F. Engelbrecht, R. Helbig: Phys. Rev. B 48, 15698 (1993)

List of Figure Captions

Figure 1 Radial wave functions (a.u.) of usual and plasmonic atoms. The parameter $R_a = \sqrt{2}r_B$ or $R_a = R_0$. The solid line corresponds to an ordinary atom and the dotted line, to the plasmonic atom.

Figure 2 Plasmon frequencies for triaxial nanoellipsoid for $n = 3$ as a function of aspect ratio a_3/a_1 for $a_2/a_1 = 0.6$. Different colors denote different values $m=1, 2, \dots, 7$.

Figure 3 Surface charge distribution (a. u.) for a plasmonic atom in triaxial metallic nanoellipsoid for $n = 3$ and $m = 7$. The ratios of ellipsoid semi-axes $a_2/a_1 = 0.7$ and $a_3/a_1 = 0.4$.

Figure 4 Normal modes (a.u.) corresponding to the six major absorption peaks of a cube [27].

Figure 5 Geometry of a two-sphere cluster.

Figure 6 Spectrum of plasmon oscillations in a two-sphere cluster for $m = 1$ for different modes L, M, T = 1, 2, 3 as a function of distance between the spheres.

Figure 7 Spatial distribution of electric potential of the modes with L, M, T = 1 in x - z plane. a, Case $m = 0$. b, Case $m = 1$. Radii of the spheres, $R_0=50$ nm; distance between their centers, $R_{12}=105$ nm. Surface of the nanospheres is denoted by a dotted line.

Figure 8 Surface charge (a.u.) of different modes with L, M, T = 1, 2, 3 at $m = 1$. Radii of the spheres $R_0=50$ nm; distance between their centers, $R_{12}=105$ nm. Surface of the nanospheres is denoted by the dotted line.

Figure 9 Plasmonic molecules in the gap between nanobubbles in metal.

Figure 10 Approximation of nonspherical nanoparticles with equivalent spherical ones, which allows to estimate properties of plasmonic molecules.

Figure 11 Plasmonic molecules in the gap between two hyperboloids. a, Geometry of the problem. b, Spectra for $m = 0$ and $L, M = 1, 3, 5, 10$.

Figure 12 Spatial distribution of wave functions for localized plasmonic oscillations in the gap between two hyperboloids for $m = 0$ and $L, M = 1$. Distance between hyperboloids, $2d=5$ nm; the least curvature radius is 50 nm (cf. Fig. 7a). Solid line depicts surfaces of hyperboloids; dotted line corresponds to the cluster of two nanospheres with $R_0 = 50$ nm and $R_{12} = 105$ nm.

Figure 13 Illustration of attraction and repulsion of the nanospheres due to different plasmonic states.

Figure 14 Van der Waals energy of two-sphere cluster defined by different plasmonic states versus distance between the spheres.

Figure 15 Relative radiative decay rate of a molecule located between two nanospheres versus the radiation wavelength. a, Nanospheres made of sodium (Na). b, Nanospheres made of silica-carbone (SiC). In both cases, $R_0 = 50$ nm and $R_{12} = 105$ nm. Direction of the molecular dipole moment is shown by arrow. The dielectric constant for Na is borrowed from [43], for SiC, from [44].

Figure 16 Excitation of plasmonic molecules in clusters of nine nanospheres with usual molecules. a, Usual and plasmonic molecules are not excited. b, External field with horizontal polarization excite the usual molecules. c, Radiation of usual molecules excite the plasmonic molecules with horizontal polarization.

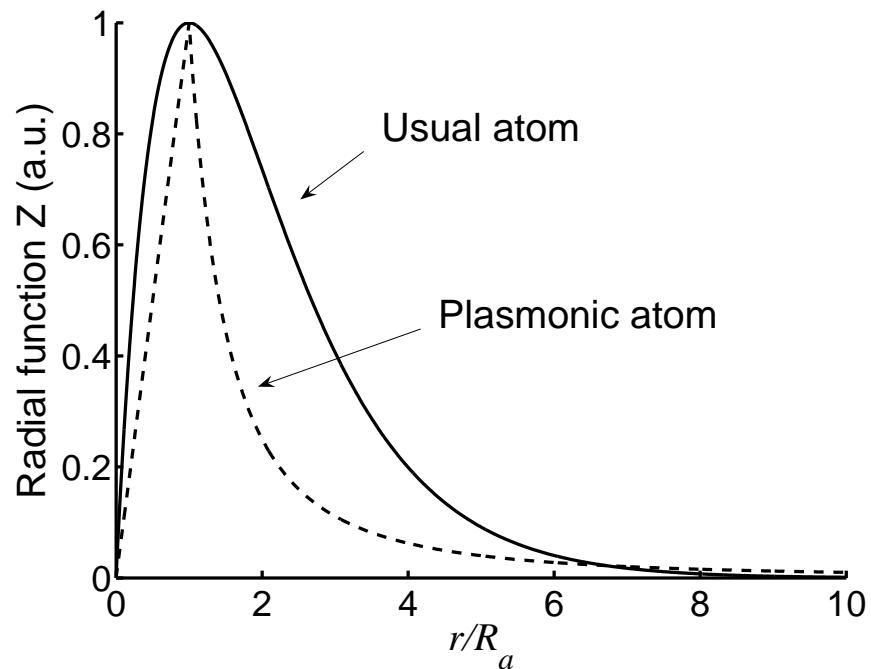


FIG. 1:

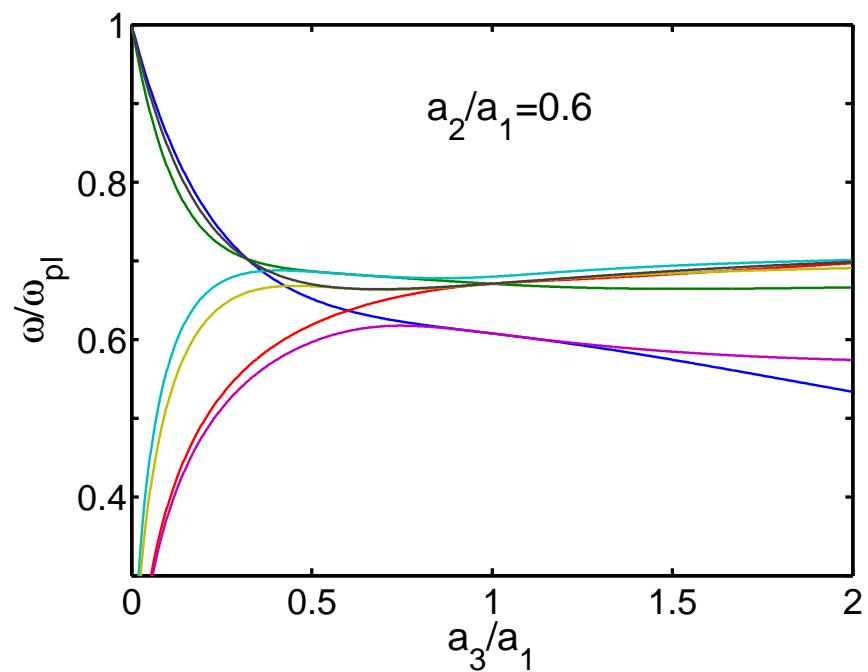


FIG. 2:

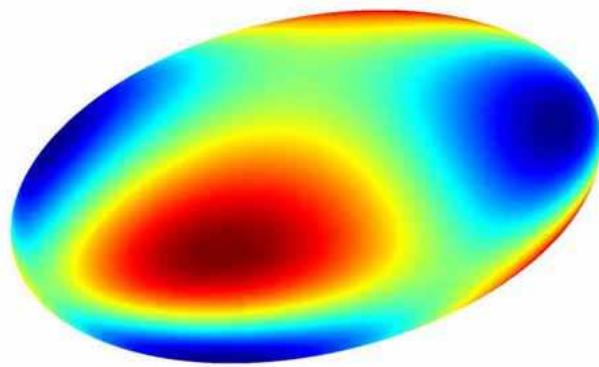


FIG. 3:

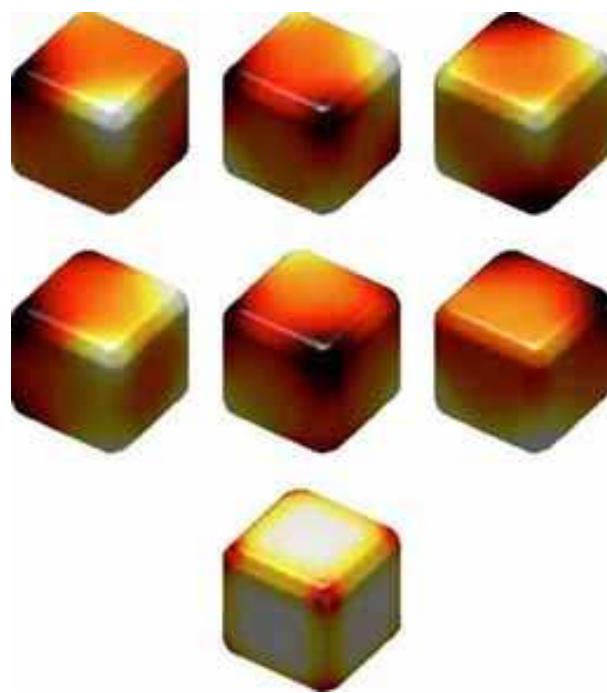


FIG. 4:

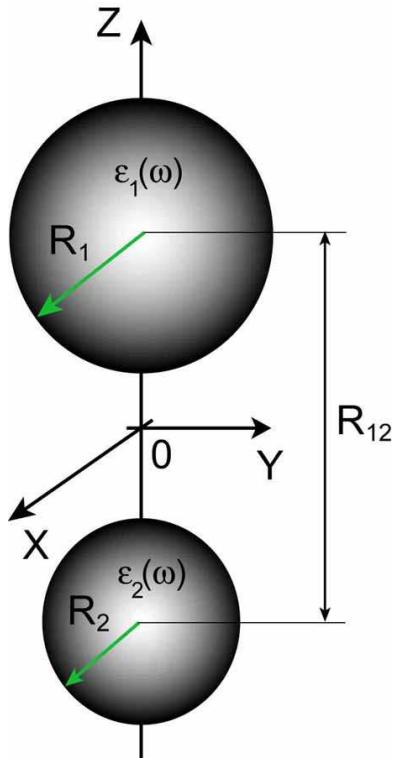


FIG. 5:

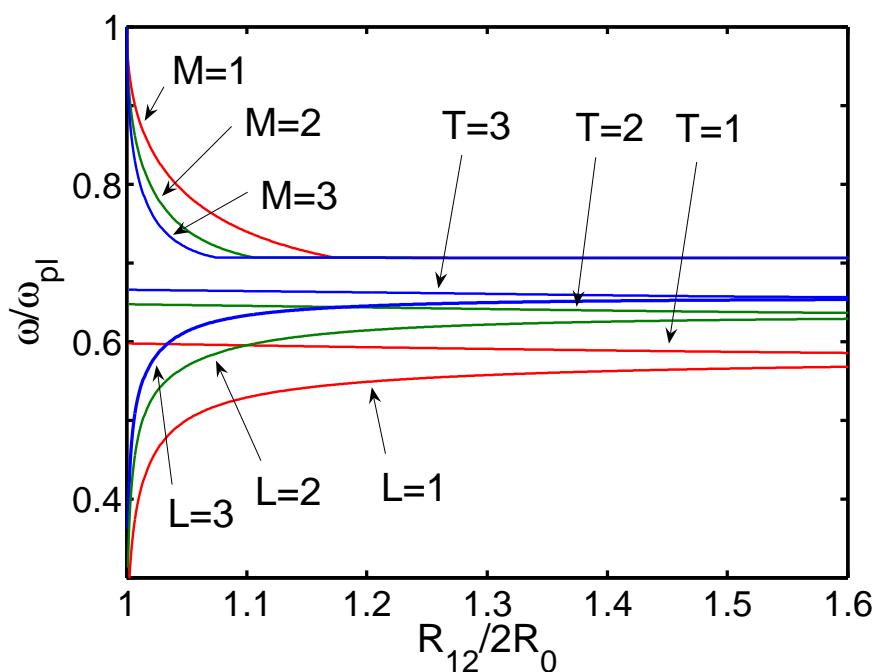


FIG. 6:

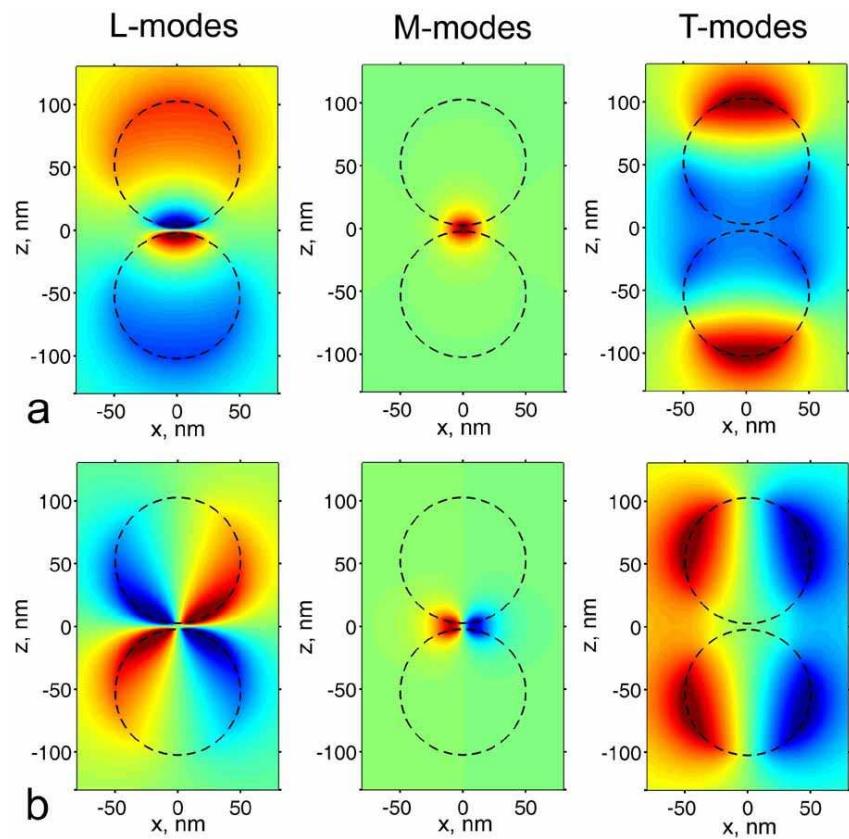


FIG. 7:

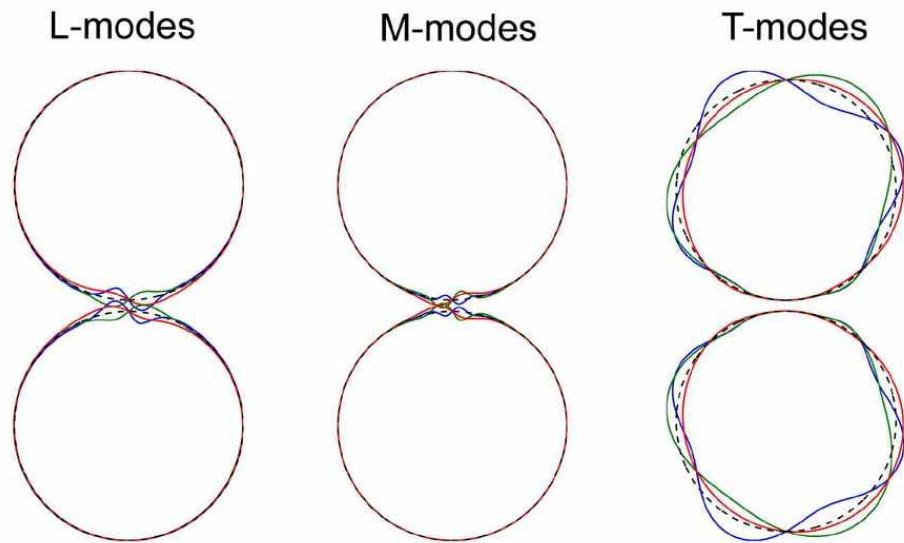


FIG. 8:

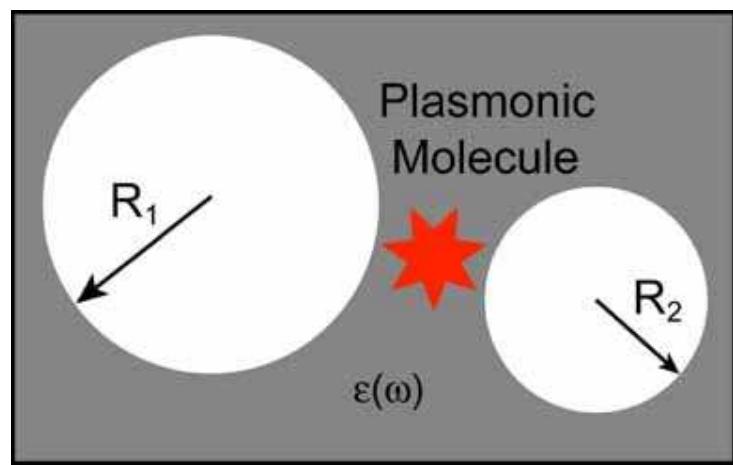


FIG. 9:

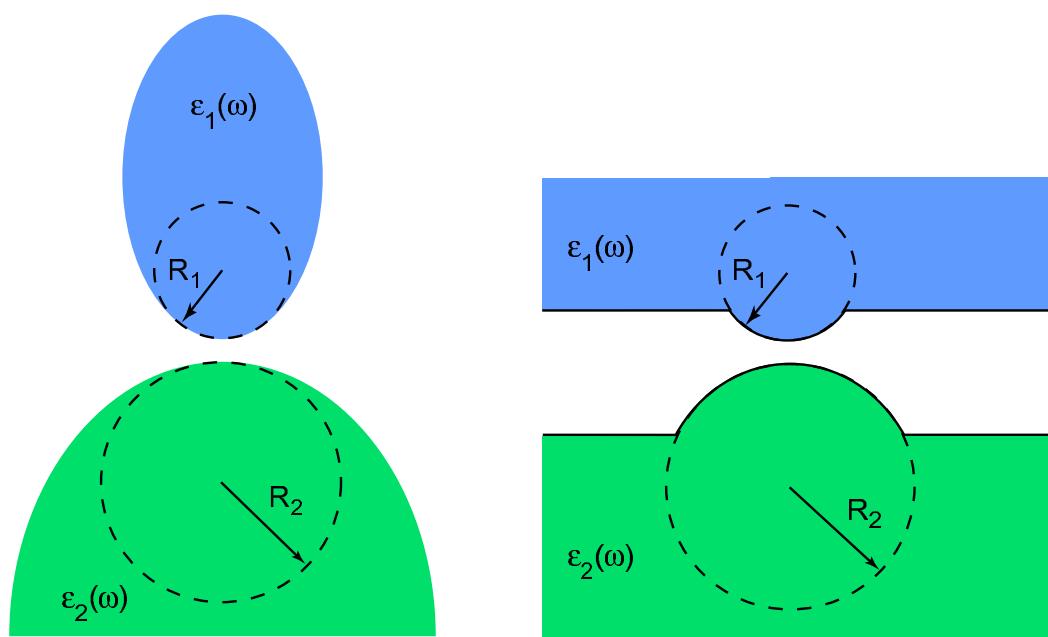


FIG. 10:

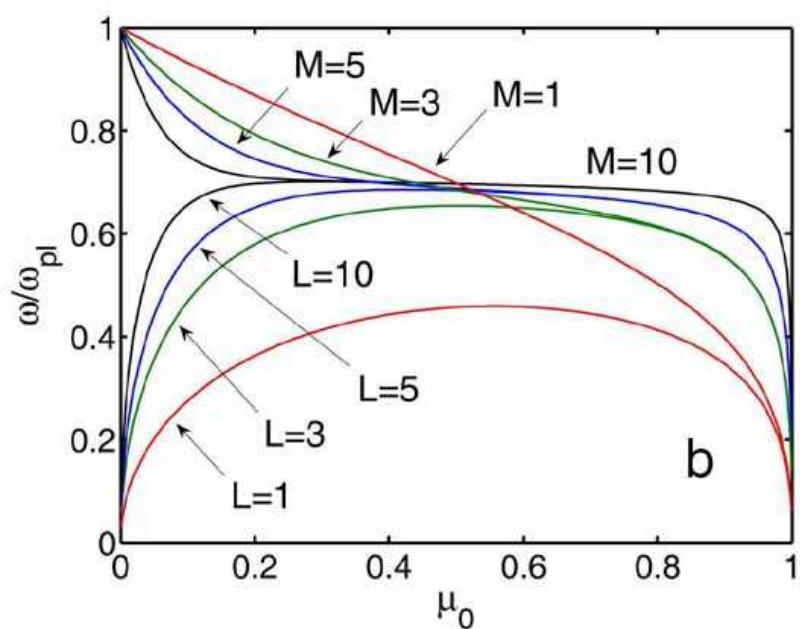
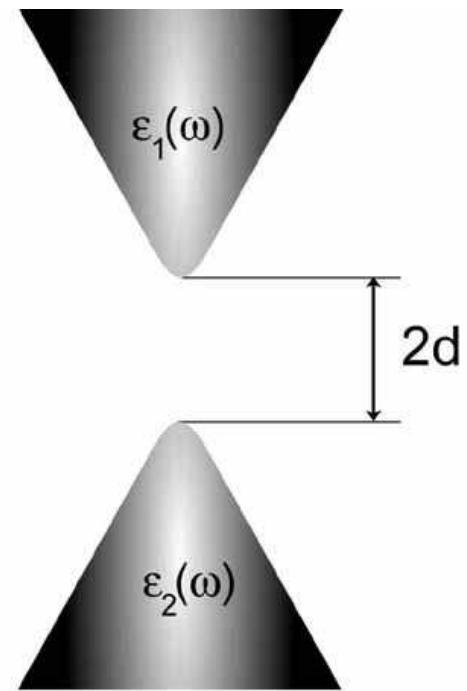


FIG. 11:

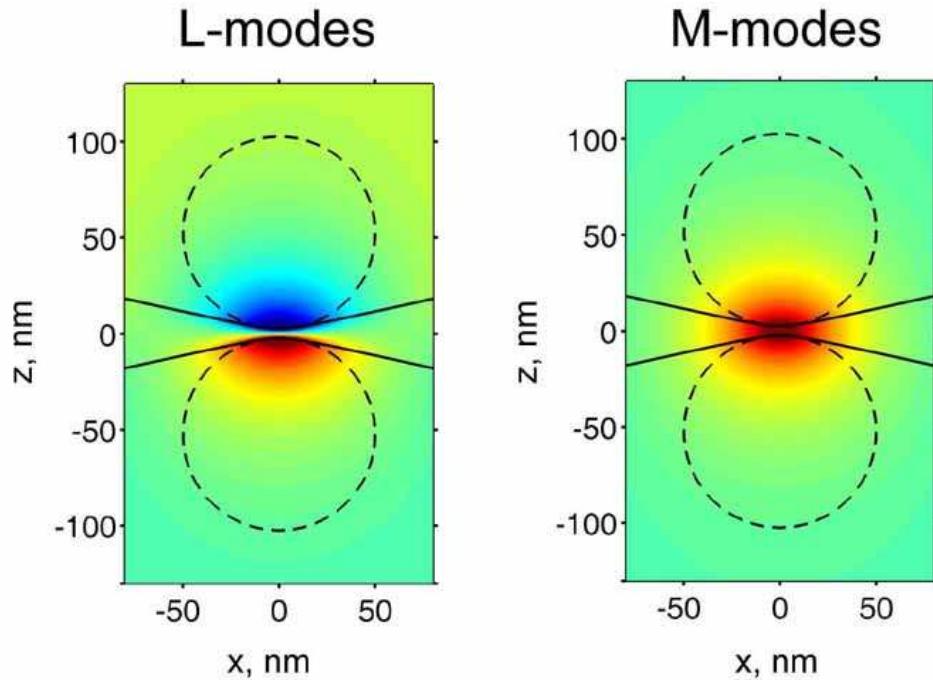


FIG. 12:

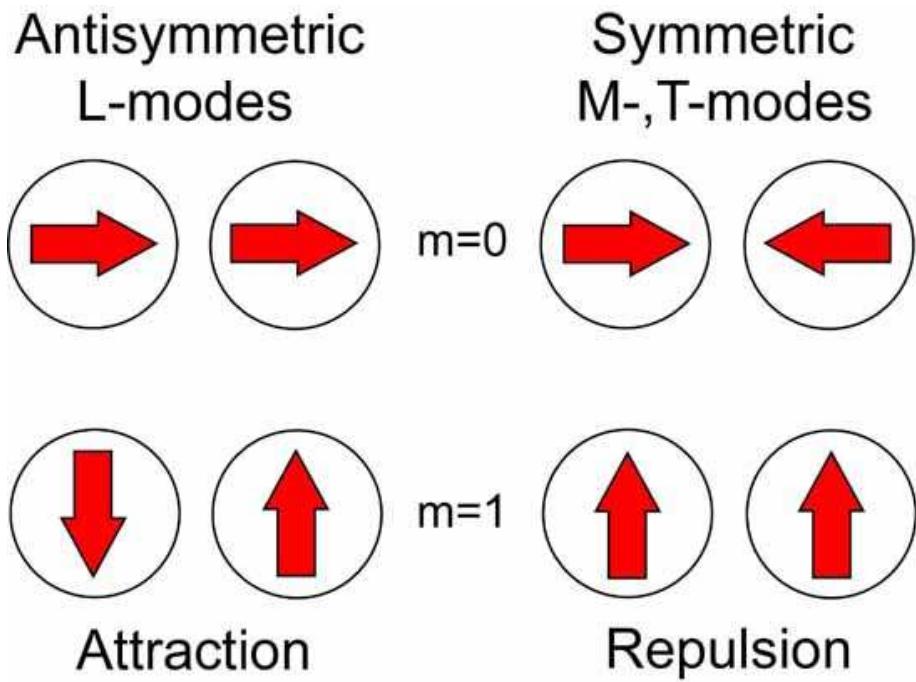


FIG. 13:

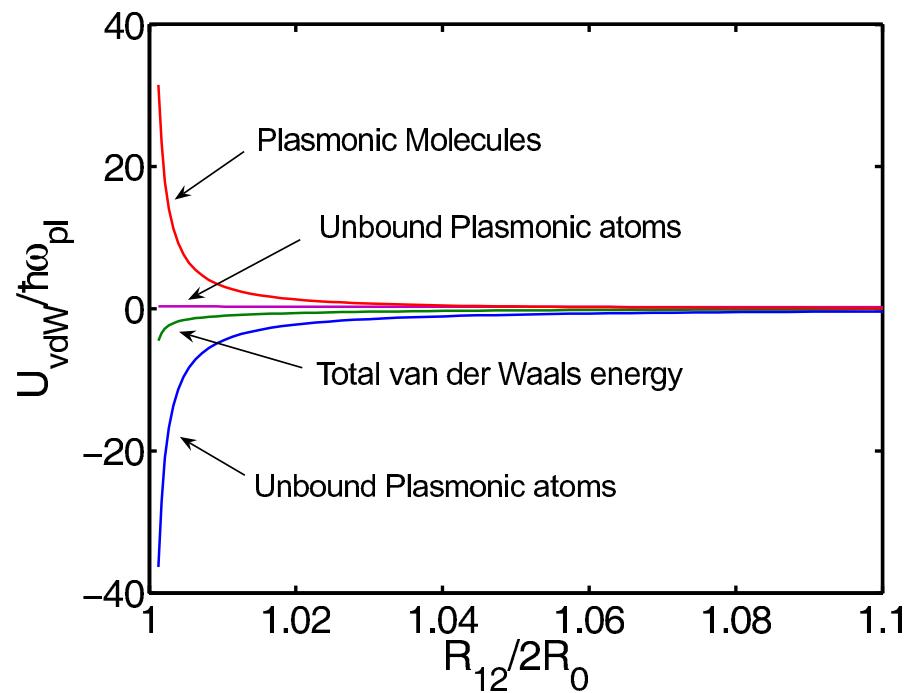


FIG. 14:

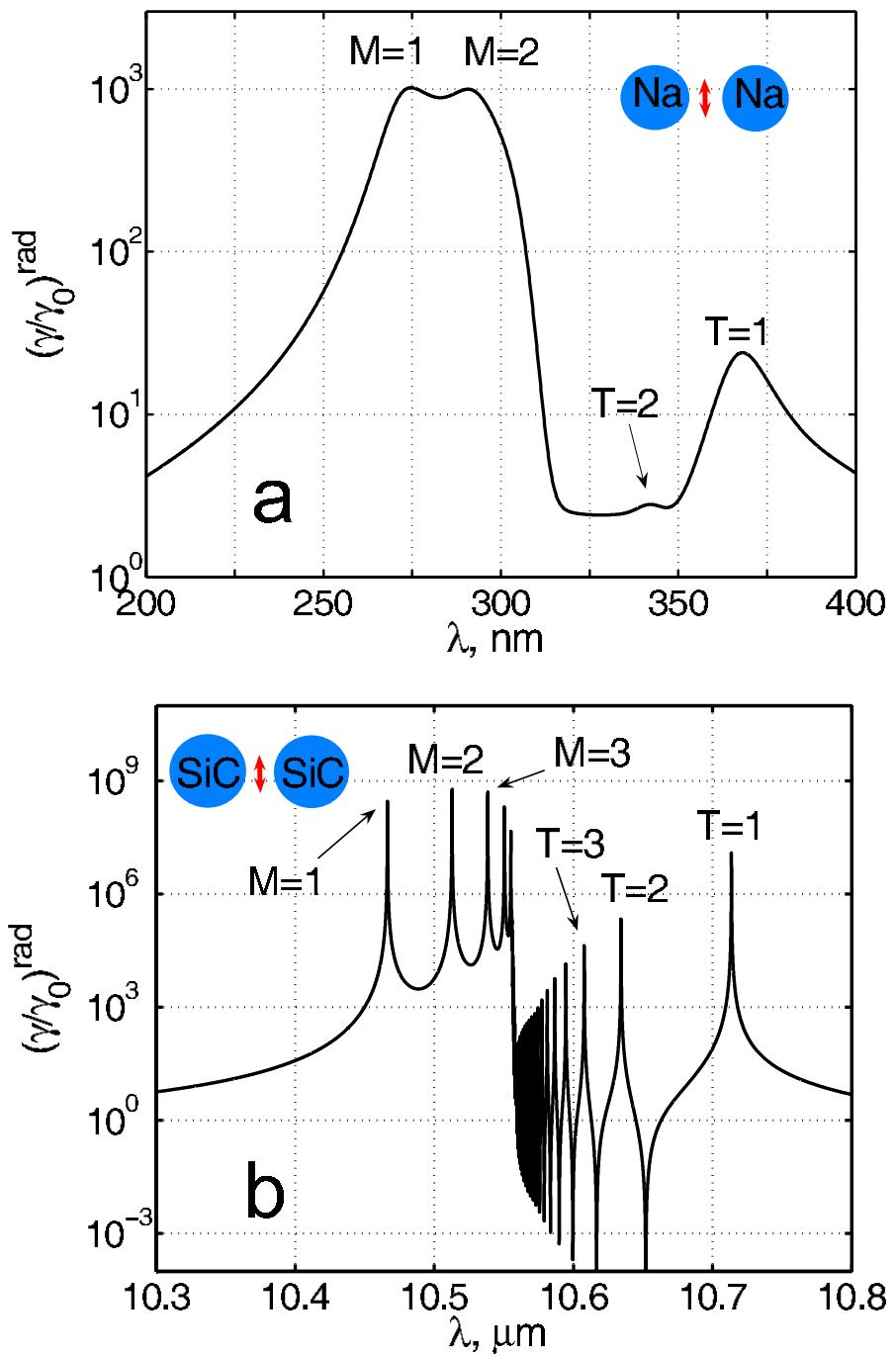


FIG. 15:

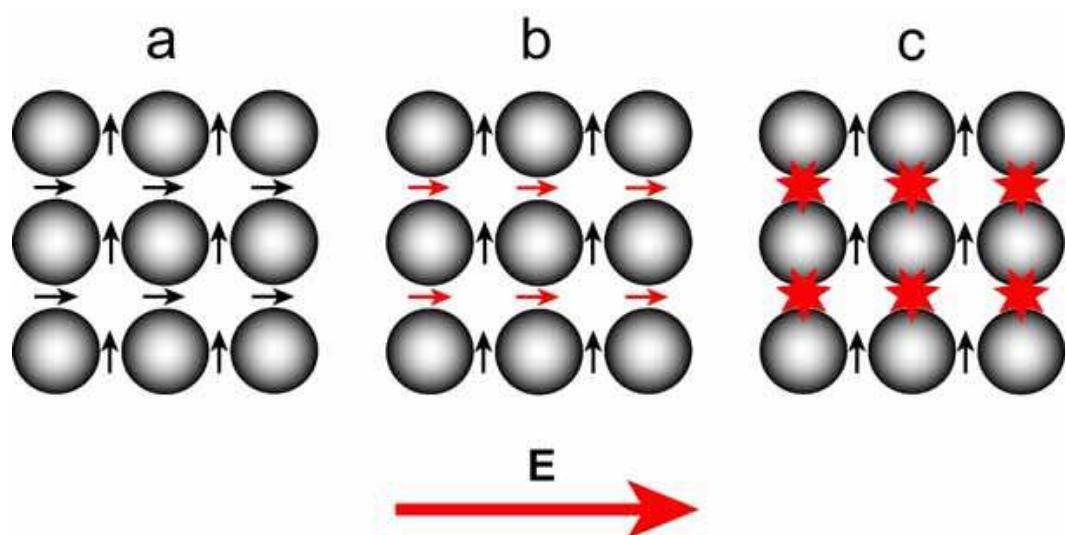


FIG. 16: